

[54] **LIQUID PHASE OXIDATION PROCESS**

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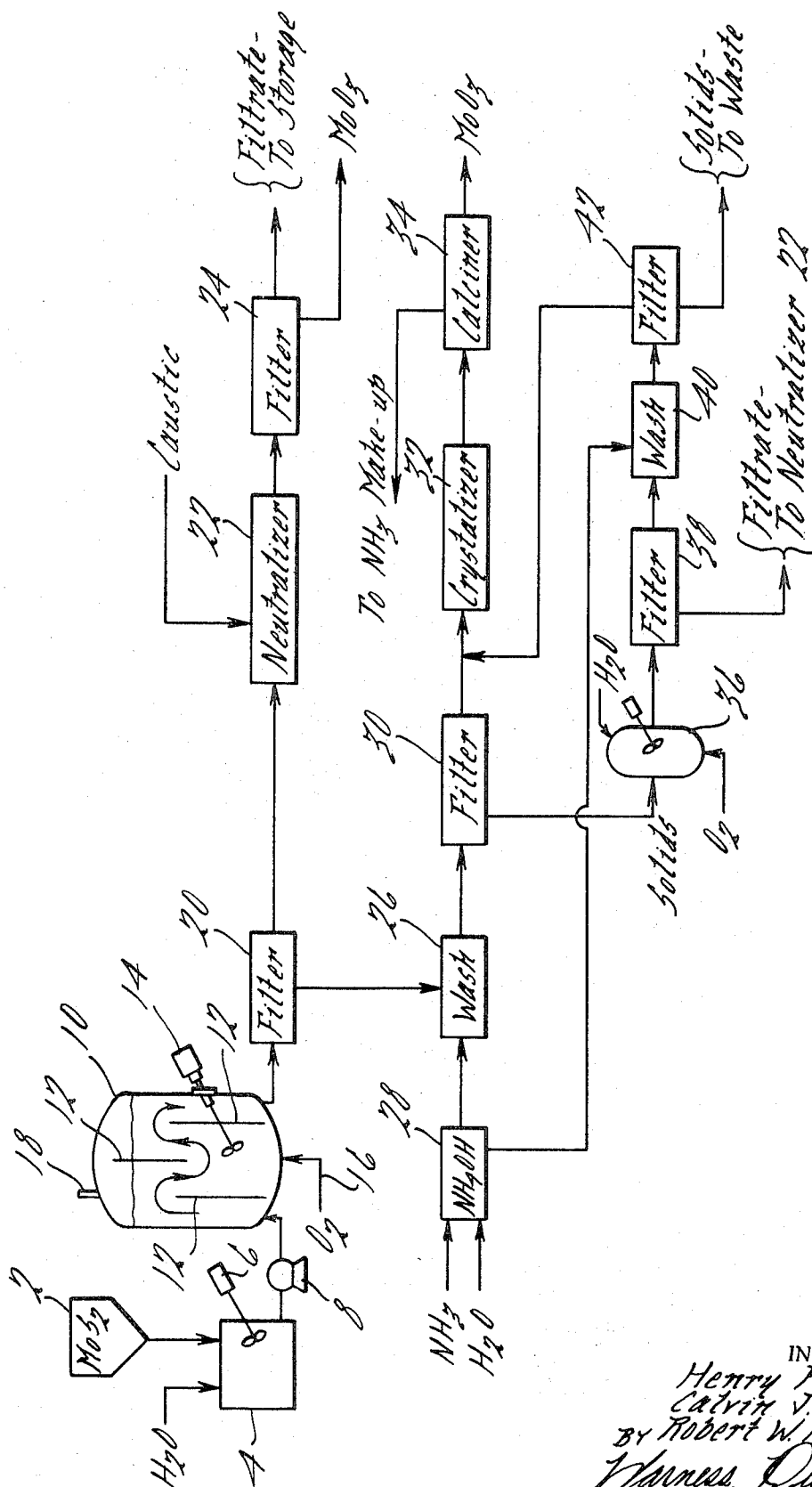
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[57] **ABSTRACT**

A process for effecting an aqueous liquid phase oxidation of molybdenum disulfide to molybdenum oxide by agitating, at elevated temperature, a slurry of molybdenum disulfide particles in water, under pressure, in the presence of oxygen for a period of time sufficient to effect the conversion of at least a portion of the molybdenum disulfide to molybdenum oxide, and thereafter extracting the molybdenum oxide product from the reaction medium.

7 Claims, 1 Drawing Figure



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LIQUID PHASE OXIDATION PROCESS

BACKGROUND OF THE INVENTION

Molybdenum does not occur as a free element in nature and is principally found in the earth's crust in the form of molybdenite (MoS_2). Molybdenite somewhat resembles graphite in appearance but has a specific gravity of about 4.5 to about 5.0 and is in the form of soft, hexagonal, black flaky crystals. One of the principal sources of molybdenite exists at Climax, Colorado, in which the ore body consists of an altered and highly silicified granite with about half the gangue being quartz through which the molybdenite is distributed in the form of very fine veinlets. The molybdenite concentration in the ore as mined usually is in the order of about 0.6 percent which, through known beneficiation processes, provides for a further concentration of the molybdenum disulfide constituent to amounts generally upwards of about 80 percent by weight.

Such ore beneficiation processes conventionally comprise a grinding operation by which the ore is reduced to a particle size usually less than about 200 mesh and wherein the particles are subjected to a flotation extraction operation using a hydrocarbon oil, such as pine oil or petroleum oil, in combination with wetting agents to effect a separation of the molybdenum disulfide constituent from the gangue.

While some of the molybdenum disulfide, after further purification, is employed directly in the compounding of lubricants, the predominant portion is converted to the oxide form in which it is employed as an alloying constituent in various metal alloys or is further reduced from the oxide form to the pure metallic state for special uses.

It has heretofore been conventional to subject such molybdenite concentrates to a roasting operation, effecting a conversion thereof to the oxide form. For this purpose, circular open hearth-type furnaces such as the Herreshoff furnace, had been employed in which the molybdenite is heated in the presence of excess air to form molybdenum trioxide and sulfur dioxide as a gaseous by-product.

The present invention provides for an improved oxidation process for effecting a conversion of molybdenum disulfide to the corresponding oxide whereby the sulfur by-product constituent can be recovered as a sulfate and the molybdenum constituent is recovered as the trioxide. In accordance with this improved process, it is now economically feasible to effect a liquid phase oxidation of molybdenum disulfide to provide molybdenum trioxide of high purity and in commercially acceptable yields.

SUMMARY OF THE INVENTION

The benefits and advantages of the present invention are achieved by forming an aqueous slurry consisting of finely particulated particles containing molybdenum disulfide dispersed in water which is heated to a temperature preferably in excess of about 80° C. under an atmosphere containing free oxygen at an oxygen partial pressure of preferably at least about 50 p.s.i. The slurry is subjected to agitation sufficient to maintain a substantially uniform dispersion of the particles through the aqueous medium and to further effect entrainment and dissolving of the free oxygen in the aqueous medium for reaction with the surfaces of the molybdenum disulfide particles. As the reaction progresses, sulfur oxides are formed, which in turn form sulfuric acid that effect a progressive reduction in the pH of the reaction medium as the reaction continues. The reaction is continued for a period of time, normally about one to six hours, depending on the specific temperature-pressure-particle size conditions employed, whereafter the molybdenum trioxide product can be separated from the acidic aqueous medium, such as by filtration.

It is usually preferred to subject the extracted solids to a wash with ammonium hydroxide, effecting a conversion of the molybdenum oxide to ammonium molybdate and leaving a solid residue consisting of unreacted molybdenum disulfide and other insoluble impurities such as the gangue. The solid

residue, if desired, can be subjected to further liquid phase oxidation to effect conversion of the balance of the molybdenum disulfide to molybdenum oxide. The resultant ammonium molybdate solution can be concentrated, such as in an evaporator, and the crystals can thereafter be subjected to calcination, providing a relatively pure grade of molybdenum trioxide.

Further benefits and advantages of the present invention will become apparent upon a reading of the description of the preferred embodiments taken in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

The drawing comprises a diagrammatic flow sheet of the process for effecting a liquid phase oxidation of molybdenum disulfide to molybdenum oxide in accordance with the preferred embodiments of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The molybdenum disulfide starting material, as previously indicated, may comprise a concentrate as derived from flotation extraction operations in which molybdenum disulfide is usually present in amounts in excess of 80 percent by weight and is in the form of finely divided particles of a size usually less than 200 mesh. Concentrates of the foregoing type derived directly from the ore beneficiation process are in the form of wet oily masses which usually contain up to about 5 percent water and up to about 7 percent of the hydrocarbon flotation oils employed in the flotation extraction operation. Such concentrates ordinarily require no pretreatment prior to oxidation in accordance with the practice of the present invention, although in some situations, it has been found advantageous to remove the predominant portion of the flotation oils to provide for increased efficiency in the oxidation reaction. This is particularly true when only a single-pass liquid phase oxidation reaction is employed. The removal of the flotation oils or a reduction in the quantity thereof can be achieved, for example, by retorting the concentrate, effecting a volatilization and/or thermal degradation and decomposition of the oils, providing a resultant substantially dry concentrate usually containing less than about 0.5 percent oil and, more usually, less than about 0.1 percent. The retorting operation is conventionally carried out at a temperature of about 1,200° F., which also effects a corresponding reduction in the water content of the concentrate. Alternatively, the concentrate can be subjected to solvent washing for removing the flotation oils followed by filtration to recover the de-oiled molybdenite.

While such molybdenite concentrates consist predominantly of molybdenum disulfide, about 5 percent to about 10 percent silica is also normally present. Other metals are also present in minimal quantities such as lead, copper, zinc, iron, aluminum, calcium, magnesium, etc. The presence of such contaminating metals, which are present in amounts of less than 1 percent, does not detract from the efficiency of the liquid phase oxidation process comprising the present invention. In those instances, however, where a substantially pure molybdenum oxide product is desired free from such trace quantities of contaminating metals, it is contemplated that the concentrate can be subjected to further leaching so as to effect an extraction of one or more of such metals with any one of a variety of techniques well known in the art.

In any event, the concentrate as derived from the mine, or as derived after further pretreatment, is of an average particle size of less than about 200 mesh and can be employed directly in forming an aqueous dispersion without further comminution. While particle sizes of less than about 200 mesh are satisfactory for the practice of the process of the present invention, it is generally preferred that the concentrate have an average particle size of less than about 20 microns, and preferably less than about 5 microns, due to the increased surface area which further promotes the efficiency of the oxida-

tion reaction. Particles of such smaller size also facilitate the formation and maintenance of a substantially uniform aqueous dispersion and are usually preferred for this purpose.

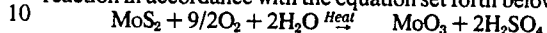
In accordance with the present process, the molybdenum disulfide concentrate, as shown in the drawing, is discharged from a storage hopper 2 into a dispersion tank 4 provided with an agitator 6 for effecting the formation of an aqueous dispersion or slurry which is intermittently or continuously transferred by means of a pump 8 into the inlet side of an autoclave 10. Depending upon the particular particle size of the molybdenum disulfide concentrate, slurries which contain up to about 40 percent by weight of molybdenum disulfide based on the total weight of the slurry can be formed. However, at concentrations at or above about 40 percent, the slurry becomes excessively thick, occasioning problems in its pumping and agitating and also its inhibiting effect on the entrapment of oxygen in the slurry to effect the liquid phase oxidation reaction. In view of the foregoing, lower concentrations, generally within the range of from about 10 percent to about 30 percent by weight molybdenum disulfide based on the total weight of the slurry, are preferred. While concentrations of the molybdenum disulfide concentrate of less than about 10 percent can also be satisfactorily employed, such lower concentrations are generally undesirable from an economical standpoint due to the excessive dilution of the material and the corresponding reduction in processing capacity occasioned by such lower concentrations. In view of the foregoing, best results are usually obtained when the molybdenum disulfide concentrate is employed in aqueous dispersions containing from about 10 percent to about 30 percent by weight of the concentrate.

In accordance with the process as diagrammatically illustrated in the drawing, the liquid phase oxidation in the autoclave 10 can be carried out batchwise and also, preferably, in a continuous manner as shown. In batch operations, it is convenient to form the dispersion directly in the autoclave, while in continuous operation, it is preferred to form the dispersion exteriorly of the autoclave employing a dispersion tank 4, as shown in the drawing, from which the slurry is continuously added to the inlet side of the autoclave and passes in a serpentine manner, as provided by the baffles 12, to the outlet side thereof. As shown, the autoclave 10 is further provided with an agitator 14 of the mechanical mixing type for maintaining a substantially uniform dispersion of the particles in the aqueous medium. Alternative agitation devices can be satisfactorily employed in lieu of the mechanical propeller-type agitator 14, illustrated in the drawing, including, for example, sparger-type agitators through which the free oxygen-containing gas is admitted under pressure into the autoclave in the form of a stream of bubbles, imparting turbulence to the aqueous medium, as well as effecting a contact of the free oxygen with the surfaces of the molybdenum disulfide particles. Conventionally, a combination of mechanical and sparger-type agitators have been found satisfactory for providing a degree of agitation sufficient to effect the continued dispersion of the molybdenum disulfide particles and also to effect an entrainment of minute bubbles of free oxygen in the aqueous medium for reaction with the surfaces of the molybdenum disulfide particles. The agitation of the slurry also promotes a mechanical scrubbing of the particle surfaces for removing the film of molybdenum oxide formed thereon, thereby exposing fresh molybdenum disulfide for further reaction with free oxygen.

The provision of free oxygen in the autoclave 10 can be accomplished by introducing pure oxygen gas through a supply line 16 or, alternatively, can be provided by air or a mixture of the two. Additional free oxygen is continuously or intermittently supplied to the autoclave to replenish that consumed during the oxidation reaction. When air is employed as the source of free oxygen replenishment, it is preferred to provide a vent line 18 in the upper portion of the autoclave for continuously and/or intermittently withdrawing gas from the upper portion of the autoclave to avoid the formation of an atmosphere which is excessively rich in nitrogen. The autoclave,

as shown in the drawing, is operated preferably from about one-half to about three-fourths full with slurry, providing a vapor space at the upper end containing free oxygen which becomes dissolved and entrained in the aqueous reaction media.

In accordance with the foregoing arrangement, the particles of molybdenum disulfide dispersed in water under heat and pressure and in contact with free oxygen undergo an oxidation reaction in accordance with the equation set forth below:



The rate of conversion of the molybdenum disulfide to the corresponding molybdenum oxide and sulfuric acid products increases as the temperature of the reaction medium increases, as the pressure of the free oxygen increases and as the particle size decreases, exposing a greater total surface area of the molybdenum disulfide per unit weight. Reaction temperatures at or around room temperature (22° C.) have been found to result in only a minimal oxidation of the molybdenum disulfide resulting in conversions of only about 1 or 2 percent of the total charge within reasonable reaction times. At higher temperatures, and particularly at temperatures in excess of about 80° C., the reaction takes place more quickly and, for this reason, temperatures of at least about 100° C. are usually employed. Best operation within normal equipment limitations has been attained by employing temperatures within a preferred range of from about 150° C. to about 250° C. The uppermost temperature limitation that can be employed is dictated by the limitations of the bursting strength of the equipment and ultimately by the critical temperature of water.

At oxygen pressures at or about atmospheric pressure, the oxidation reaction has been observed to be very slow and totally impractical from a commercial standpoint. It has been discovered that as the partial pressure of the free oxygen is increased to above about 50 p.s.i., a marked improvement in the rate of reaction and in the product yield takes place. Particularly satisfactory results are attained employing oxygen partial pressures of from about 300 p.s.i. up to about 600 p.s.i. or above. While oxygen partial pressures in excess of about 600 p.s.i. have been found to provide for further improvements in the reaction rate, the increases in reaction rate at these higher levels become progressively smaller and are not significantly greater than that attained at pressures at or about 600 p.s.i. Additionally, oxygen partial pressures in excess of about 600 p.s.i. require that the processing equipment employed be of substantially greater structural strength, and it is because of the foregoing considerations that the use of such higher pressures is not ordinarily economically justified.

In accordance with the foregoing, the liquid phase reaction medium preferably comprises an aqueous dispersion containing from about 10 percent up to about 30 percent by weight of molybdenum disulfide particles of an average particle size of less than about 200 mesh which is vigorously agitated at a temperature preferably ranging from about 150° C. to about 250° C. in contact with free oxygen present at a partial pressure of from about 300 p.s.i. to about 600 p.s.i. Under the foregoing conditions, substantially complete reaction and conversion of the molybdenum disulfide to the corresponding oxide takes place within about one to about six hours.

At the completion of the reaction, the acid aqueous slurry is withdrawn from the autoclave and is transferred, as shown in the drawing, to a filter 20 for effecting a separation of the molybdenum trioxide reaction product from the filtrate. The filter cake also contains unreacted molybdenum disulfide particles and any other solid contaminating material such as the gangue present in the original concentrate which is predominantly in the form of silica. The aqueous filtrate which is acidic due to the presence of the sulfuric acid formed during the oxidation reaction also contains some dissolved molybdenum in the form of molybdenyl sulfate. The acidity of the filtrate conventionally ranges from a pH of about 0 to a pH of about 2.0, depending upon the concentration of molybdenum disulfide in the original slurry charge and the extent to which the conversion reaction has taken place.

The filtrate discharged from the filter 20 is preferably transferred, as shown in the drawing, to a neutralizer 22 in which an alkaline compound, such as caustic, is added and causes precipitation of the dissolved molybdenum trioxide. The precipitated molybdenum oxide can be recovered in a filter 24. The neutralized filtrate from the filter 24 can be suitably discharged to storage and subsequently utilized as a source of sulfate.

It is also contemplated in accordance with the practice of the present invention that a portion of the filtrate from the filter 20 can be recycled back to the autoclave or to the tank 4 used for preparing the slurry prior to charging the autoclave. Generally, however, the recycling of such acidic filtrate causes the initial slurry charge to be slightly on the acid side, resulting in an increased acidity of the reacted slurry as withdrawn at the output end of the autoclave. For this reason, while a recycling of a portion of the filtrate from the filter 20 can be accomplished, generally the quantity recycled is small. In accordance with the preferred practice, all of the filtrate is directly transferred to the neutralizer 22.

The filter cake derived from the filter 20 consists of a precipitated molybdenum trioxide product in combination with unreacted molybdenum disulfide and a small proportion of inert contaminants, such as silica, originally introduced with the molybdenum disulfide concentrate. An extraction of the molybdenum trioxide product from the filter cake is conveniently achieved by transferring the filter cake to a wash treatment 26, in which it is subject to an aqueous ammonium hydroxide wash solution prepared in a make-up tank 28. The aqueous ammonium hydroxide wash solution may range in concentration from about 1 to about 12 normal (N), and preferably, concentrations of about 10 to 12 N are used in order to minimize water dilution of the resultant molybdate solution. The quantity of wash solution employed is designed to provide a molar ratio of ammonia to molybdenum of preferably at least 2.3 up to about 3.0. The wash solution effects a dissolving of the molybdenum oxide by converting it to ammonium molybdate. The unreacted molybdenum disulfide and solid contaminants are thereafter removed in a filter 30 and the filtrate containing the dissolved ammonium molybdate can be concentrated, such as by evaporation or in a crystalizer 32, as shown in the drawing. The solid ammonium molybdate derived from the crystalizer can be employed as a product in that form or, alternatively, can be transferred to a calciner 34 in which it is heated, effecting an evolution of ammonium gas which is recycled back to the ammonium hydroxide make-up tank 28. The resultant molybdenum trioxide product is of high purity.

The filter cake derived from the filter 30 containing unreacted molybdenum disulfide in combination with inert contaminants is preferably accumulated and thereafter charged to a second autoclave 36 in which an aqueous slurry is formed and a further oxidation reaction is carried out in accordance with the reaction as previously described in connection with the autoclave 10. The autoclave 36 similarly is provided with appropriate agitation and means for introducing oxygen under pressure to effect a conversion of the residual molybdenum disulfide to the corresponding oxide with a formation of sulfuric acid in accordance with the reaction equation as hereinbefore set forth. The reacted slurry is transferred from the autoclave 36 to a filter 38 in which the precipitated molybdenum trioxide particles are removed in combination with the contaminating inert particles along with any residual unreacted molybdenum disulfide. The filtrate from the filter 38 may conveniently be transferred to the neutralizer 22 at which it is treated with caustic in a manner as previously described. The resultant filter cake from the filter 38 similarly is washed with an aqueous ammonium hydroxide solution, effecting a dissolving of the molybdenum trioxide product in a treating tank 40, whereafter it is transferred to a filter 42 for removal of the undissolved solids which comprise essential inert contaminating materials originally present in the molybdenum disulfide concentrate. The filtrate from the filter 42 is conveniently trans-

ferred and is mixed with the filtrate from the filter 30 for further concentration in the crystalizer 32 in a manner as previously described.

In accordance with the process as hereinbefore described, a substantially complete conversion of molybdenum disulfide to molybdenum trioxide of relatively high purity can be achieved in a commercially economical manner and wherein the residual solid and liquid waste products can be harmlessly disposed of by conventional disposal means. The efficiency of the liquid phase oxidation process in the first autoclave is evidenced by the attainment of yields of converted molybdenum trioxide based on the original molybdenum content of the concentrate as charged usually in excess of 80 percent. The efficiency of conversion can be further improved by employing a multiple-phase reaction as exemplified by the continuous autoclave 10 and wherein any residual unreacted molybdenum disulfide is subsequently substantially completely converted to the oxide form using an auxiliary autoclave 36. In order to further illustrate the process comprising the present invention, the following examples are provided. It will be understood that the examples are provided for illustrative purposes and are not intended to be limiting of the scope of the invention as set forth in the subjoined claims.

EXAMPLE I

A regular grade molybdenum disulfide concentrate derived from an oil flotation extracted molybdenite ore from Climax, Colo., having an average particle size of less than 200 mesh was employed for the liquid phase oxidation reaction. The concentrate was washed 6 times with acetone to remove the residual oils and was thereafter dried for several hours at a temperature of 110° C. The chemical analysis of the de-oiled concentrate revealed that it contained 52.44 percent molybdenum and 35.54 percent sulfur with a sulfur to molybdenum mole ratio of 2.03:1.

A 1-liter capacity autoclave equipped with a magnetically driven agitator was employed for the liquid phase oxidation reaction. A slurry was prepared by mixing 50 grams of the molybdenum disulfide concentrate with 450 grams of water and charging the resultant slurry into the autoclave. The autoclave was pressurized with oxygen and thereafter heated, during agitation, to the operating temperature. Heating was continued to provide a substantially constant operating temperature of about 177° C. (350° F.) with a total vapor pressure of 750 p.s.i. gauge of which the calculated oxygen partial pressure was about 615 p.s.i. Since initiation of the reaction occurs during the heat-up period, a replenishment of the oxygen consumed during the heat-up period as well as during the course of the reaction at operating temperature was achieved by connecting the upper portion of the autoclave in communication with a cylinder containing pure oxygen set at the selected total pressure of 750 p.s.i.g. The reaction was carried out for a period of 6 hours under continued agitation employing a tubular stirrer shaft adapted to pull vapor from the vapor space above the liquid slurry down through the stirring shaft, effecting a distribution thereof at the lower portion of the slurry, thereby assuring intimate contact of the molybdenum disulfide particles with free oxygen. Agitation was controlled so as to maintain a substantially uniform slurry of the particles and to assure adequate gas-solid contact during the course of the reaction.

At the completion of the reaction, the charge was cooled and filtered through a Buchner funnel and the filter cake was dried for several hours at 110° C. The filtrate, at the completion of the reaction, was at a pH of less than zero. Thirty grams of the dry filter cake thereafter was stirred with 250 milliliters of 5 N ammonium hydroxide for 30 minutes at room temperature, effecting a dissolving of the molybdenum oxide and the charge was thereafter filtered and the residue again dried at 110° C. and weighed. The yield of molybdenum oxide was calculated based on the original filter cake recovered and the weight loss of the ammonium hydroxide-washed filter cake

which revealed a conversion of about 88.4 percent of the molybdenum disulfide to molybdenum trioxide.

EXAMPLE II

A second test was conducted employing the same concentrate and equipment as previously described in connection with Example I. The same procedure utilizing the same temperature and reaction conditions, but a total pressure of 350 p.s.i.g., was used, providing a calculated oxygen partial pressure of 215 p.s.i. The resultant filtrate had a pH of 0.12 and an analysis of the reaction residue revealed a conversion of molybdenum disulfide to molybdenum trioxide of about 81 percent based on the original charge.

EXAMPLE III

A third test was conducted employing the same concentrate and equipment as previously described in connection with Example I. The same procedure utilizing the same temperature and reaction conditions were used but a total pressure of 1,500 p.s.i.g. was employed so as to provide a calculated oxygen partial pressure of 1,365 p.s.i. The resultant filtrate obtained had a pH of less than zero and analysis of the reaction residue revealed that 89.8 percent of the molybdenum disulfide present in the original charge was converted to molybdenum trioxide.

EXAMPLE IV

Still another test was conducted in which the same starting material and apparatus was employed as previously described in connection with Example I. In this specific run, however, air rather than pure oxygen was employed to initially pressurize the autoclave to a total pressure of 750 p.s.i.g., providing a calculated oxygen partial pressure of 120 p.s.i. Replenishment of oxygen as consumed during the reaction was accomplished in the same manner as described in Example I. At the completion of a 6-hour reaction period, the filtrate was observed to have a pH of 0.26 and analysis of the reaction residue revealed a conversion of molybdenum disulfide to molybdenum trioxide

of about 54.1 percent based on the molybdenum disulfide in the original concentrate charged.

While it will be apparent that the description of the preferred embodiments of the process comprising the present invention will achieve the benefits as hereinbefore set forth, it will be understood that the invention is susceptible to modification, variation and change without departing from the spirit of the invention.

What is claimed is:

1. A process for converting molybdenum disulfide to molybdenum oxide, which comprises the steps of dispersing a particulated molybdenum disulfide-bearing material having an average particle size less than about 20 microns in water forming an aqueous slurry containing up to about 40 percent by weight of said material, heating said slurry to a temperature of at least about 80° C. and agitating said slurry while in contact with an atmosphere containing free oxygen at an oxygen partial pressure of at least about 215 p.s.i. for a period of time sufficient to effect the conversion of a major portion of the molybdenum disulfide to molybdenum oxide and sulfur oxide acid products accompanied by a progressive reduction in the pH of said slurry, and thereafter recovering the molybdenum oxide product from said slurry.
2. The process as defined in claim 1, wherein said particulated molybdenum disulfide-bearing material is of an average particle size less than about 200 mesh.
3. The process as defined in claim 1, wherein said atmosphere comprises air.
4. The process as defined in claim 1, wherein said atmosphere comprises substantially pure oxygen.
5. The process as defined in claim 1, wherein said slurry is heated to a temperature ranging from about 150° C. to about 250° C.
6. The process as defined in claim 1, wherein said oxygen partial pressure is at least 300 p.s.i.
7. The process as defined in claim 1, wherein said slurry contains from about 10 percent to about 30 percent by weight of said particulated molybdenum disulfide bearing material.

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